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Cross-shaped mesogens in main chain polymers

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Cross-shaped mesogens in main chain polymers

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The synthesis of semiflexible main chain polyesters with cross-shaped mesogens and their phase behaviour, investigated by polarizing microscopy, DSC and X-ray diffraction, is presented. Polyesters of this type show mesophases with dominating nematic character and relatively high clearing temperatures. Systematic variation of the spacer and the terminal groups of the mesogens shows that longitudinally fixed rod-like parts of the mesogens have a strong influence on the clearing temperature and, therefore, on the mesophase behaviour. The corresponding rod-like but laterally fixed parts of the cross-shaped mesogens influence the melting temperatures significantly. This is critical in determining crystallization. However, laterally fixed rod-like parts contribute also to the formation of mesophases, but clearly to a far less extent.

1. Liquid-crystalline polymers with combined structural principles

The combination of the classical liquid crystal architectural principles resulted in the so-called combined polyesters (I) which are composed of elements of the classical main chain and side group polymer [1]. They show broad mesophases; the type of liquid-crystalline phase is significantly dependent on the length of the spacer groups. Newer combinations are composed of laterally and longitudinally attached mesogens as shown by (II) [2] and (III) [2–4]. Whereas the first examples of type II exhibit monotropic mesophases at best, polyesters of type III are enantiotropic and show mesophases at relatively low temperatures. The influence of the spacer group dominates the structure–property relationships for this class of mesomorphic polyesters.

If the spacer is omitted (IV) [2, 5, 6] in polyesters of type III or is incorporated again in another way (V), liquid-crystalline (cf. **8a** [5]) and non-mesomorphic polyesters (cf. also **P30** in [6]) are created, depending on the detailed chemical structure. As depicted by (V), the laterally attached mesogen crosses the second, semiflexible linked mesogen in the main chain. Model compounds [7] and polyesters [5] with cross-shaped mesogens have shown mesomorphic behaviour. Results are presented here which reveal the influence of various structural elements on the phase formation.

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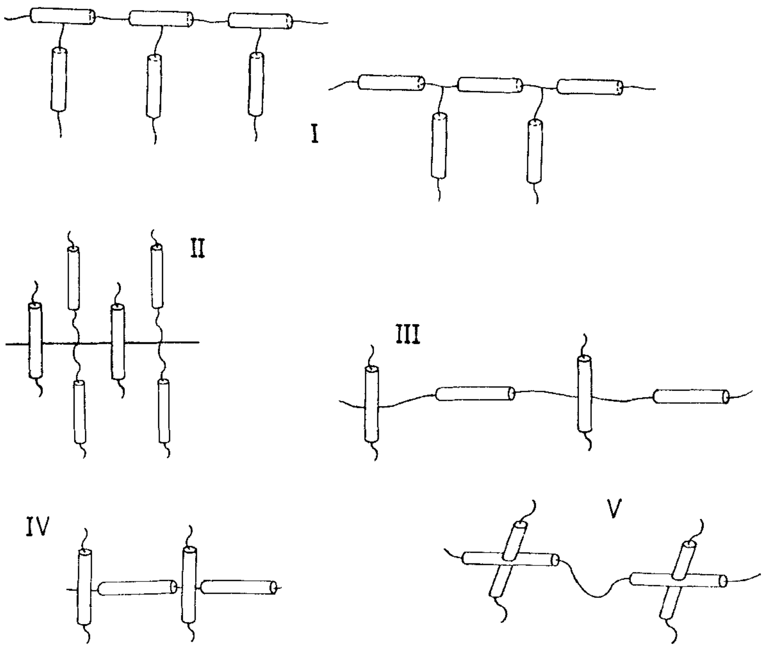

2. Synthesis

Polyesters with cross-shaped mesogens were synthesized via condensation of dibenzoyloxy-dihydroxy-benzene derivatives [6, 7] (**A** + **B**) with an α,ω-bis(4-chloroformyl-phenoxy)alkane [8] (see scheme 1). That 4,6-dibenzoyloxybenzene-1,3-diol derivatives **B** were not incorporated into the polyesters, leading possibly to the appropriate 2,5-dibenzoyloxybenzene-1,4-diol [7] by transesterification, was clearly proved only for a low molecular weight model compound (ester **31** in scheme 3 [7]) via X-ray analysis. For the polyesters described here, it was not possible to perform single crystal X-ray diffraction for that purpose. However, several additional important indications exist which imply that the condensation to the polyesters **P31–P44** (table 1) occurs in the same way as in this low molecular case, and that subsequently only the 2,5-dibenzoyloxybenzene-1,4-diols (**A**) were incorporated into the polyesters **C**:

(*a*) All polyesters except **P37** with branched terminal groups at the mesogens crystallize at least after a short time of annealing. On incorporation of a higher amount of 4,6-dibenzoyloxybenzene-1,3-diols (**B**) the symmetry of the polymer chain (**D**) is disturbed and rapid crystallization is improbable.

(*b*) With the help of X-ray diffraction on crystallized and liquid-crystalline fibres, it was found that all of the polyesters have the same liquid-crystalline and the same crystalline phase (see later). This should be expected only when the structures of the polyesters are comparable and do not vary in the composition of the different repeating units (**C** and **D**).

(*c*) The pronounced dependence of the clearing and melting temperatures (see later) on either the length of the spacer *or* the length of the terminal groups of the laterally fixed mesogens are easier to understand with structure **C**. With a mixed structure or with structure **D** the difference between spacer and terminal groups becomes indistinct.

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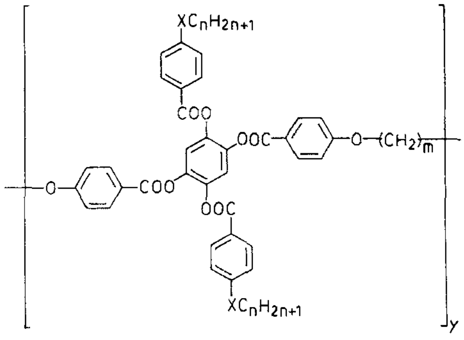
Table 1. Molecular weights and phase behaviour of polyesters with cross-shaped mesogens.



Polyester	X	n	m	M_{GPC}	M_W	P_W	U	Phase behaviour§/°C	ΔH_{NI}/J g^{-1}
P31	—	1	5	60000	64000	93	2·2	g 91 C† 202 (N 181) I	4
P32	0	1	5	42000	46000	64	2·2	g 79 C† 201 N 238 I	4
P33	0	2	5	30000	34000	46	1·8	g 76 C 213 N 236 I	4
P34	0	3	5	49000	53000	68	2·2	g 67 C 188 N 223 I	4
P35	0	4	5	81000	89000	111	2·1	g 68 C 197 N 228 I	4
P36	0	5	5	56000	67000	81	2·0	g 53 C† 126 N 192 I	3
P37	0	5‡	5	36000	61000	73	2·6	g 75 C† N‡ 150 I	2
P38	0	12	5	35000	38000	37	2·4	g 37 C† 95 N 131 I	2
P39	0	4	2	100000	99000	130	2·1	g 83 C 261 N 286 I	7
P40	0	4	3	45000	49000	63	1·9	g 76 C† 170 N 200 I	4
P41	0	4	4	112000	120000	152	2·2	g 54 C 187 N 269 I	7
P35	0	4	5	81000	89000	111	2·1	g 68 C 197 N 228 I	4
P42	0	4	6	74000	77000	94	2·0	g 57 C 199 N 249 I	7
P43	0	4	9	58000	61000	71	2·0	g 44 C 168 N 191 I	4
P44	0	4	10	44000	48000	55	1·9	g 34 C 177 N 194 I	5

† Crystallization occurs upon annealing.
‡ (−)2-methylbutoxy terminal groups at the mesogens, causing possibly a cholesteric phase.
§ Values determined by DSC, heating rate: 20°C/min.

Because of these arguments, only the formula **C** is used further for the polyesters **P31–P44**. Independent of the exact repeating unit, the mesogens are nevertheless cross-shaped.

Verification of the total configuration via NMR spectroscopy, as could be made for polyesters with laterally attached mesogens in the main chain [6], is not possible for polyesters with cross-shaped mesogens (see figure 1). Both protons of the benzene ring c in the centre of the cross are spectroscopically identical here. Whether identical benzoic acid ester groups are bound in 1,4- (see **C** scheme 1) or 2,4-position (see **D**) makes no difference to the chemical shift of the protons in 3,6-position (c).

3. Relations between structure and properties

The molecular weights and the results of DSC measurements of polyesters **P31–P44** are summarized in table 1. The dependence of the phase behaviour on molecular weight is given elsewhere [9]. Polyesters with long spacers containing even numbers of methylene groups, recrystallize faster than polyesters with short spacers containing odd numbers of methylene groups (see figure 2; compare curves with $m = 2$ and 3; 5 and

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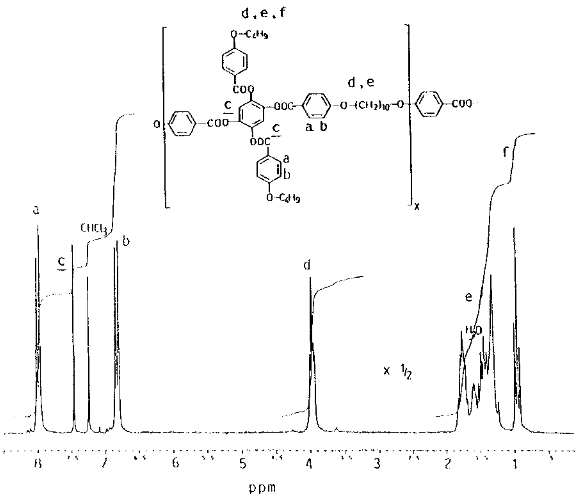

Figure 1. 200 MHz ^{1}H NMR spectrum of polyester **P43**.

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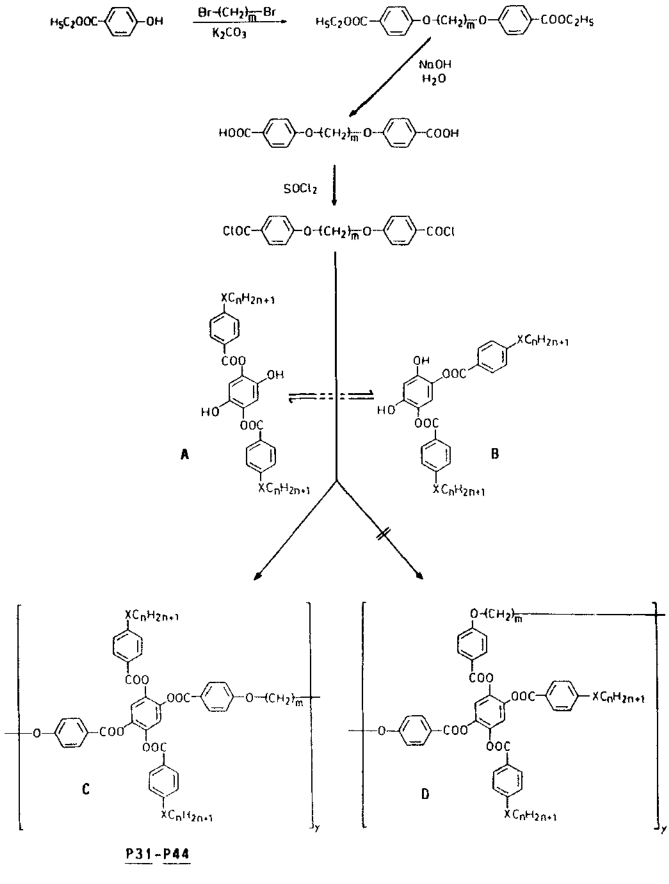

Scheme 1. Synthetic route to the polyesters with cross-shaped mesogens.

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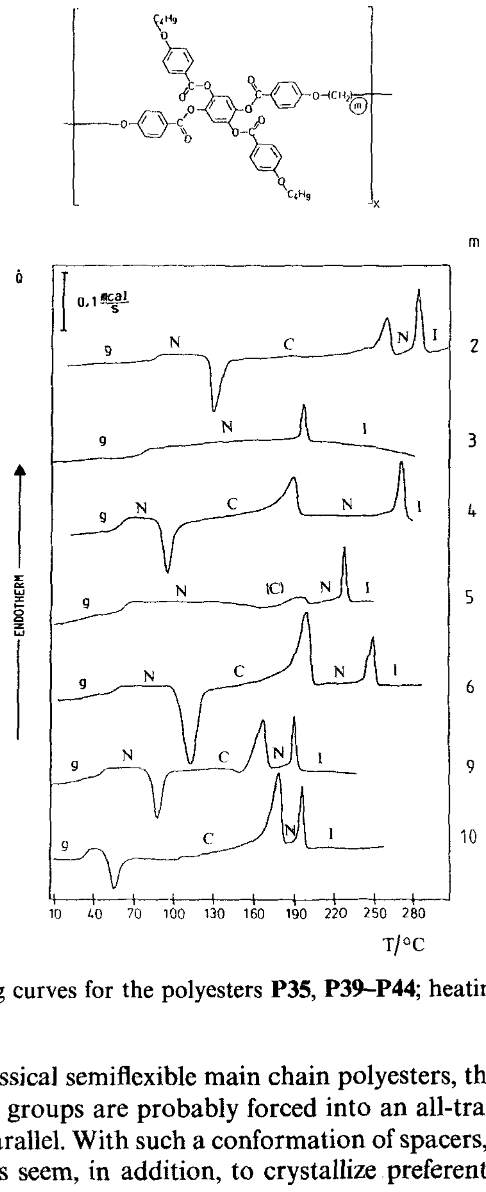

Figure 2. DSC heating curves for the polyesters **P35**, **P39–P44**; heating rate 20°C min^{-1}.

6; 9 and 10). As for classical semiflexible main chain polyesters, the spacers with even numbers of methylene groups are probably forced into an all-trans conformation to orient the mesogens parallel. With such a conformation of spacers, the polyesters with cross-shaped mesogens seem, in addition, to crystallize preferentially, at least more rapidly than polyesters with an odd number of methylene groups in the spacers. In this case gauche conformations of the spacer can be expected.

Concerning the terminal groups of the mesogens, the tendency to recrystallize is higher with an even number of carbon atoms in each terminal group as well, but decreases with increasing length of the terminal group. This is in contrast to polyesters with only laterally attached mesogens in the main chain [6] which crystallize more rapidly with long terminal groups.

In the following, conclusions can be drawn from phase diagrams showing the dependence of the transition temperatures on the spacer length (see figure 3) and on the length of the terminal groups (see figure 4): with an increasing number of methylene groups in the spacers as well as in the terminal groups, the glass, melting and clearing temperatures all decrease. Moreover, a distinct odd–even dependence of the clearing

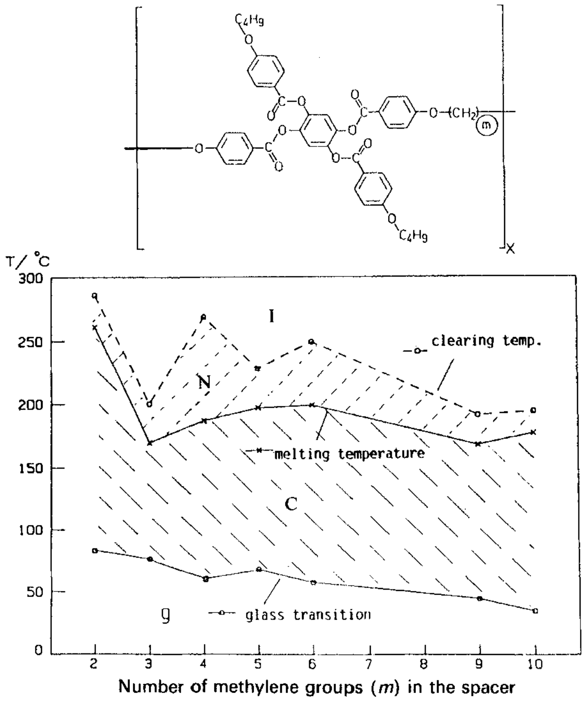

Figure 3. Variation of the transition temperatures with the length of the spacer.

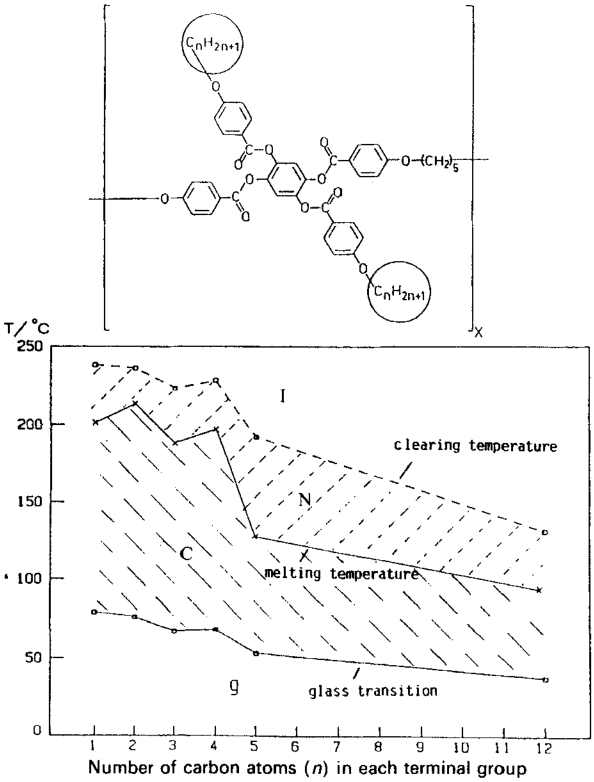

Figure 4. Variation of the transition temperatures with the length of the terminal groups of the mesogens.

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temperatures on the length of the spacer and an odd–even dependence of the melting temperatures on the length of the terminal groups are observed. In the same way as the clearing temperatures alternate, transition enthalpies at the clearing temperature also depend on the length of the spacer. Because the crystalline modification and the liquid-crystalline phase are all the same for polyesters **P31–P44**, it is concluded that

(*a*) the longitudinally attached rod-like part of the mesogenic cross imparts liquid-crystalline behaviour near the clearing temperature, whereas

(*b*) the laterally attached mesogen distinctly influences the order in the crystalline phase.

4. The type of liquid-crystalline phase

The form of the cross-shaped mesogen deviates distinctly from the usual rod-shaped mesogen; the large *p*-alkoxybenzoyloxy substituents of the longitudinally attached part of the mesogen in the main chain behave differently from conventional lateral alkyl substituents which fit close to the mesogen in the direction of the long molecular axis. In this regard, the liquid-crystalline behaviour, in part over 250°C, is remarkable. Also, the mesogens do not have an ideal disk-shape; the central benzene ring should have a six-fold substitution for this. All of the polyesters **P31–P44** show a comparable optical texture after annealing (see figure 5) and similar X-ray scattering patterns (see figure 6). The optical texture (see figure 5) develops slowly from a marbled form. Stripes are formed, reminiscent of a chevron texture of calamitic mesophases which have been observed in some cases just below a S_C–N transition [10]. But, for polyesters with cross-shaped mesogens, the optical texture exists unchanged across the entire temperature range of the liquid-crystalline phase. It may be presumed that the mesogens cannot assume a preferred nematic or smectic C phase.

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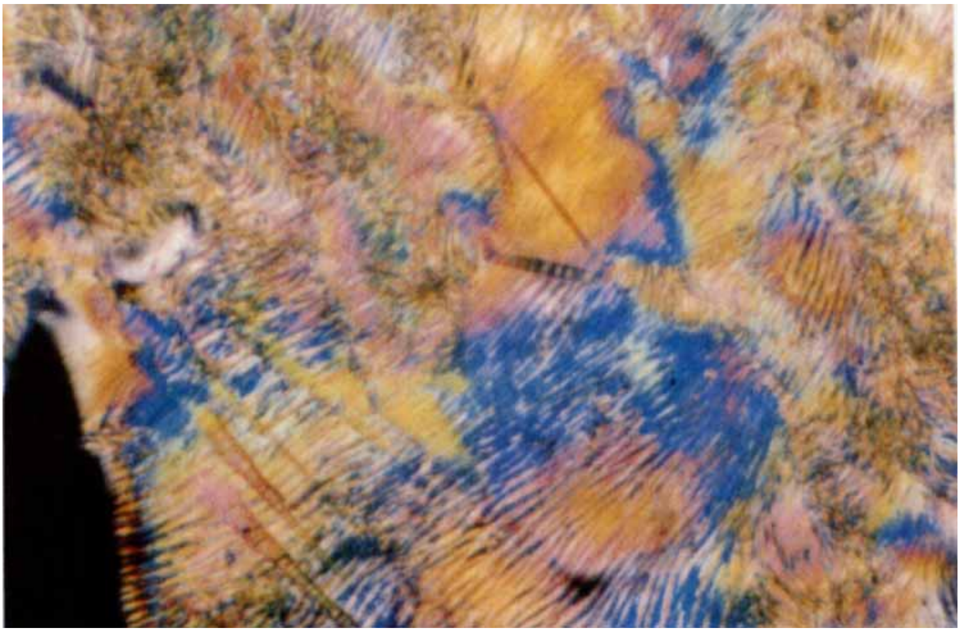

Figure 5. Typical texture in the polarizing microscope of polyesters with cross-shaped mesogens after annealing in the liquid-crystalline phase.

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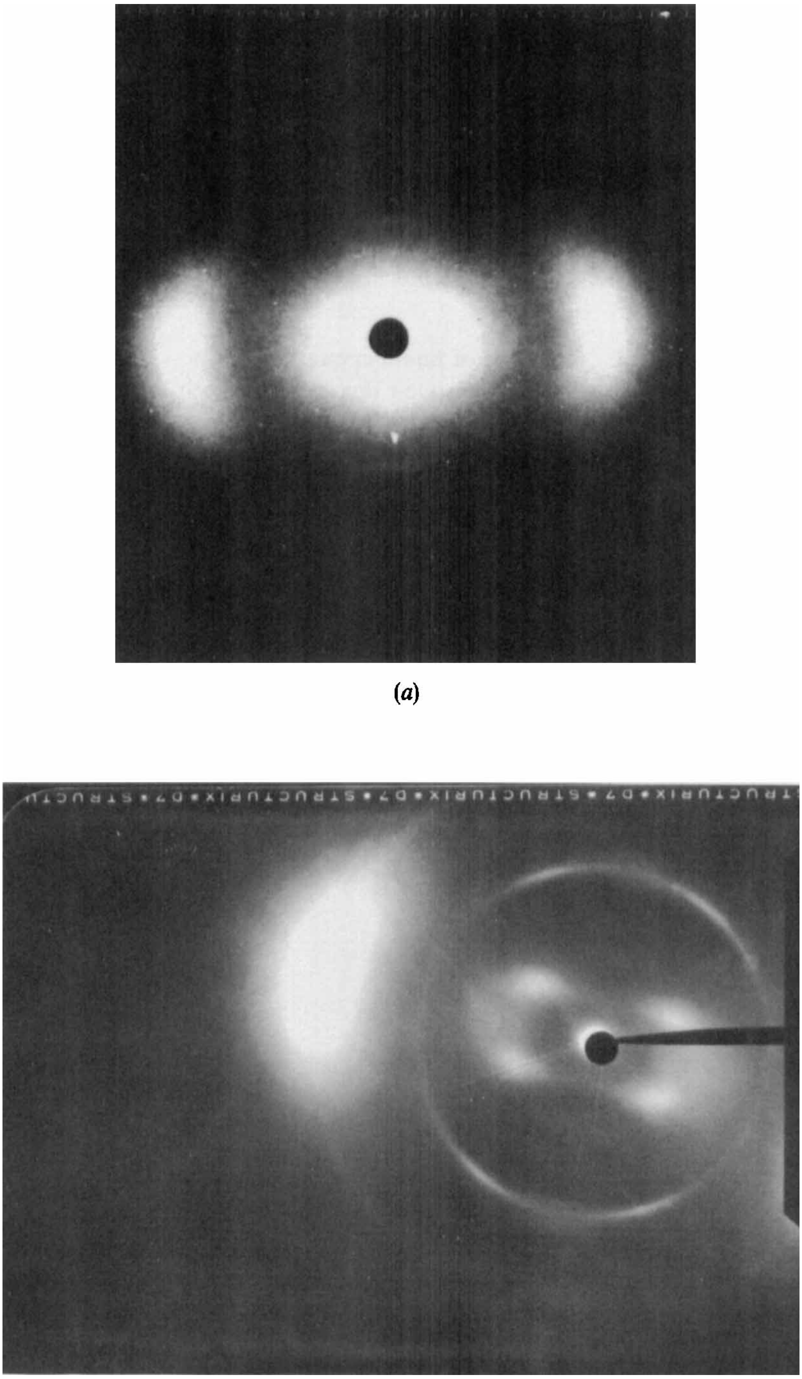
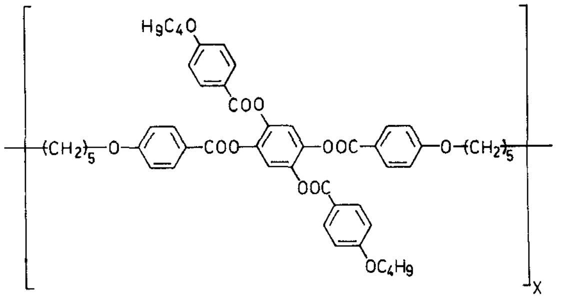


(*a*)

(*b*)

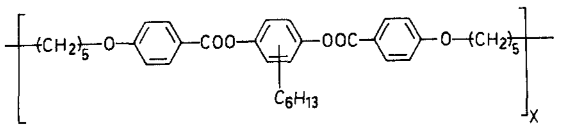
Figure 6. X-ray scattering patterns for polyester **P44** (glassy fibre at room temperature, produced from the liquid-crystalline state). (*a*) Normal flat chamber exposure. (*b*) Exposure in an evacuated flat chamber (the ring is a technically conditioned reflection, which has nothing to do with the diffraction by the fibre).

X-ray scattering patterns (see, for example, **P44**, figure 6) may be interpreted in the same way: the flat camera exposure (see figure 6(*a*)) displays a diffraction pattern typical for a calamitic nematic phase. To reduce the diffraction by air an evacuated chamber was also used (see figure 6(*b*)). Four symmetrically arranged reflections occur also, similar to the case of smectic C phases. However, the intensity compared with an original S_c is far too weak and too diffuse. Similar X-ray scattering patterns are known from calamitic, cybotactic nematic phases [11, 12]. However, an identification of the mesophase of the polyesters with cross-shaped mesogens as a cybotactic nematic remains unsatisfactory. The layer reflections of 10–13 Å in such a mesophase could not be justified in terms of the dimensions and the peculiar shape of the mesogen. But, the laterally attached part of the mesogen does not perturb the structure like an alkyl substituent. On the contrary, it contributes to stabilizing the mesomorphic behaviour as demonstrated in the following comparison. Already one hexyl group as a lateral substituent decreases the clearing temperature of the nematic phase to 86°C.



P44

g 34°C C 177°C N 194°C I



g 17°C C 75°C N 86°C I

Comparing with the polyester **P44** containing cross-shaped mesogens, a mesophase is observable until nearly 200°C. Therefore, the arrangement of the mesogens in the mesophase remains undecided. In addition, the position of the X-ray diffraction reflections are nearly independent of the terminal and spacer groups. After crystallization, the four symmetric small angle reflections also remain (see figure 7). In contrast to the liquid-crystalline phase, the position of the four reflections changes (8–15 Å), dependent upon the particular molecular structure. However, all X-ray exposures of crystallized polyesters with cross-shaped mesogens show comparable patterns, suggesting the same crystalline modification.

5. Experimental

5.1. *Polyesters **P31–P44***

The α,ω-bis(4-chloroformyl-phenoxy)alkanes were synthesized analogous to a procedure described in the literature [8]. But in contrast, analytically clean products were isolated after recrystallizing the crude products from absolute cyclohexane. Pyridine was prepared by distillation over calcium hydride and 1,1,2,2,-tetrachloroethane was fractionated over phosphorus pentoxide.

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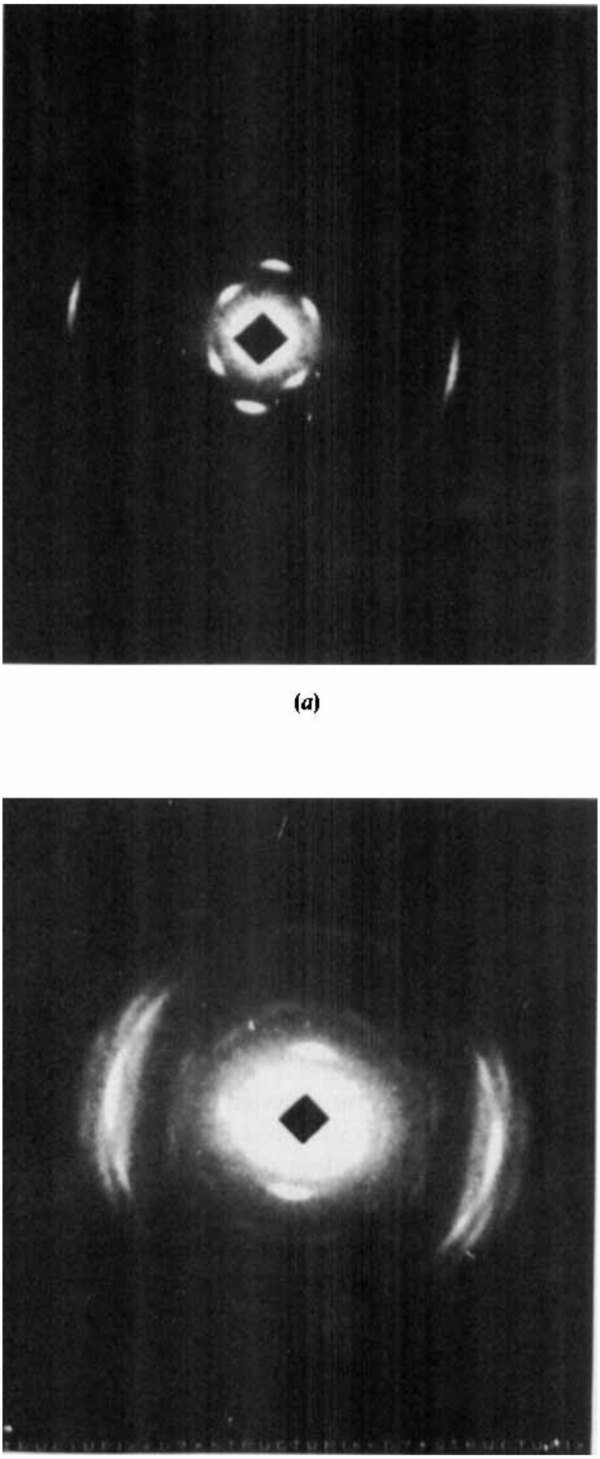

Figure 7. Flat chamber exposures of a crystallized fibre of polyester **P35** (*a*) exposed for a short time and (*b*) exposed for a long time.

Table 2. Yields and elemental analyses.

		Elemental analysis			
		Calculated		Found	
Polymer	Yield/%	%C	%H	%C	%H
P31	80	71·72	4·99	71·28	5·52
P32	93	68·59	4·77	67·81	4·72
P33	52	69·23	5·13	68·94	5·71
P34	77	69·79	5·47	69·45	5·57
P35	81	70·31	5·77	70·36	5·26
P36	74	70·91	6·07	70·88	6·47
P37	79	70·91	6·07	70·68	6·20
P38	72	73·66	7·65	72·96	7·76
P39	94	69·47	5·30	69·59	4·81
P40	71	69·76	5·46	69·49	4·99
P41	62	69·44	5·70	69·93	5·90
P42	85	70·58	5·92	70·56	5·59
P43	70	71·31	6·34	71·18	5·88
P44	71	71·54	6·47	71·56	6·53

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In a Schlenk tube about 1 mmol of the appropriate dicarbonic acid dichloride was dissolved in 3 ml of absolute tetrachloroethane. An appropriate amount of the diol in a mixture of 0·5 ml of pyridine and 2 ml of tetrachloroethane was added to the diacid dichloride solution. The tube was closed under a stream of dry argon and was stirred for 3 to 5 days. Cooling of the tubes at the beginning of the reaction was not necessary. If precipitation occurred the reaction temperature was increased until the precipitate redissolved. Afterwards the reaction mixtures were diluted with chloroform to 10 ml and precipitated dropwise in 100 ml of methanol. The polyesters were separated by centrifugation, redissolved in 10 ml of chloroform and reprecipitated again. In those cases where the polyesters were soluble in benzene, they were freeze-dried. All other polyesters were dried in vacuum to constant weight. The yields and elemental analyses of the polyesters are summarized in table 2.

5.2. *Characterization methods*

All polyesters were characterized by elemental analyses, ^{1}H NMR spectra and, in some cases, by IR spectra. The analytical GPC was carried out as described in a following publication [9]. The thermal behaviour was examined with a POL-BK II polarizing microscope (Leitz) equipped with a FP 5 hot stage (Mettler), by X-ray diffraction experiments and by a differential scanning calorimeter (DSC-2C; Perkin-Elmer). Because of the importance of the thermal history on the DSC measurements some further clarification of these methods is given elsewhere [6].

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